BRI DGMAN-SOLUTION CRYSTAL GROWTH ANI) CHARACTERIZATION OF THE SKUTTERUDITE COMPOUNDS $CoSb_3$ and $RhSb_3$

T. CAILLAT , J. -P. FLEURIAL and A. BORSHC1 IEVSKY

Jet Propulsion Laboratory

California Institute of Technology

4800 Oak Grove Drive

Pasadena CA 91109

USA

Abstract

Compounds with the skutterudite structure have recently been identified as advanced thermoelectric materials. We report on the crystal growth and characterization of the skutterudite compounds $CoSb_3$ and $RhSb_3$ which form peritectically at 873 and 900°C, respectively. Large single crystals were obtained by the vertical gradient freeze technique from solutions rich in antimony. The samples were characterized by high temperature Hall effect and electrical resi stivity measurements. A band gap of 0.56 and 0.80 eV was estimated from these measurements for $CoSb_3$ and $RhSb_3$, respectively. N-typc $CoSb_3$ samples were obtained by doping with Te. Exceptionally high p-type Hall mobility values have been measured and a room temperature value of 3445 $cm^2.V^{-1}s^{-1}$ was obtained for $CoSb_3$ at a carrier concentration of $4\times10^{17}cm^{-3}$ and 8000 $cm^2.V^{-1}s^{-1}$ was obtai ned for $RhSb_3$ at a carrier concentrate on of $3.5\times10^{18}cm^{-3}$.

1. Introduction

$CoSb_3$ and $RhSb_3$ are members of a large family of compounds which crystallize with the cubic skutterudite structure ($CoAs_3$), space group $Im3\,(T_h^5)$ and eight AB_3 groups in the unit cell [1]. The skutterudite compounds have recently been identified as candidates for advanced thermoelectric c materials [2,3,4]. Based on diamagnetism and electrical properties measurements, Hulliger concluded that skutterudite compounds were semiconductors [5]. More recent experimental and theoretical studies [3,6] also confirmed the semiconducting nature of the skutterudite compounds. Up to now almost all the properties of the skutterudite samples were measured on hot-pressed materials. Because of the interest in these materials as thermoelectric and also new semiconductors, the preparation of high quality single crystals is desirable for their characterization. We report on the preparation of single crystals of the peritectic skutterudite compounds $CoSb_3$ and $RhSb_3$. The growth of large single crystals (up to 10 mm long and 10 mm in diameter) by the gradient freeze technique is described. The crystals were investigated by X-ray techniques and also electron probe microanalysis (EPMA). Several properties of the samples were measured in a wide temperature range and the results are discussed.

2. Experimental

The compound $CoSb_3$ forms peritectically at 873°C [7]. The Co-Sb phase diagram shows that the growth of the compound can be initiated from Sb-rich melts between 91 and about 97 at.% Sb [7]. For $RhSb_3$, which forms peritectically at 900°C, the growth can be initiated from Sb-rich melts between 86 and 97 at.% Sb [8]. A two zone-furnace was used and a thermal baffle was introduced between the upper and the lower zone in order to prevent any air convection. An opening of about 12.5 mm in diameter was made in the center of this baffle to introduce the melt container. Details about the furnace used for the growth can be found in reference [9]. The growth was conducted in a sealed quartz ampoule which was stationary during the growth. The temperature close to the upper part of the thermal baffle was controlled by a temperature programmer/controller and a second temperature controller maintained a constant temperature gradient between the upper and the lower zones of the furnace. The furnace was calibrated and temperature gradient as high as 125 °C/cm were obtained near the interface. The growth process was obtained by lowering the temperature of the furnace and the temperature gradient could be adjusted by changing the difference of temperature maintained between the two zones.

Co (4N) and Sb (6N) were introduced in pointed quartz ampoules, coated with graphite and sealed under vacuum. The nominal composition of the melt was 93 at.% Sb and the total load was about 30 gins. Similarly Rh (3N) and Sb (6N) ampoules were prepared with a nominal composition of 93 at.% Sb. Doping studies were conducted for $CoSb_3$ using Te ask dopant. A temperature gradient of about 50°C/cm was maintained at the growth interface and the growth rate was about 0.7 °C/hour for both compounds. Samples were cut using a diamond saw and used for microstructure investigations as well as transport property measurements. The microstructure of the samples was investigated using an optical Nikon microscope. Some samples were ground for X-ray di ffractometry (XRD). XRD analyses were performed on a Siemens D-500 diffractometer using Cu-K_α radiation with silicon as a standard. Laue pictures were taken on several samples to determine their crystallographic orientation. Some samples were mounted in epoxy and polished to perform EPMA on a JEOL JXA-733 superprobe. The density of some samples was measured at room temperature by an immersion technique using toluene as displacement liquid. Samples were also characterized at room temperature by Hall effect and van der Pauw measurements. High temperat ure Hall effect and electrical resi stivit y measurem ents were also performed on selected samples up to about 73 O°C.

3. **Results and discussion**

3.1. Crystal growth results

Several ingots of $CoSb_3$ and $RhSb_3$ were successfull y grown and a typical ingot is shown in Figure 1. As expected, the grown ingots were composed of two parts: the lower part corresponding to the skutterudite compound and the upper part corresponding to an Sb-rich eutectic. The interface between the two phases was always clearly seen on the ingots (see Figure 1). This interface was very flat which indicates the uniformity of the temperature gradient in the furnace and in the melt as well as the temperature stability during the growth. The lower part of the ingots was cut from the rest of the ingot using a diamond saw and subject to further analysis. Density measurements on the entire lower portions of the ingots showed that the experimental densities were found to be about 99.5 % of the theoretical density of $CoSb_3$ and $RhSb_3$: 7.621 and 7.893 $g.cm^{-3}$, respective] y. XRD analysis of samples cut from the lower part of' the ingots always showed that the samples were single phase with a composition corresponding to the skutterudite structure. EPMA investigations of samples also showed that they were single phase with a composition close to 1:3 with a slight shift towards Sb which could be expected since the crystal were grown from the Sb-rich side and the boundary limit of the solidus was obtained on the Sb-rich side. EPMA of samples from the very tip and the top of the ingots did not show any compositional difference with an accuracy of $\pm$ 0.2 at.%. Investigati ons of poli shed samples revealed that the samples were crack-free and uniform in composition.

Ingots of $CoSb_3$ were composed of very large ~g-sins (a few mm) but single crystals as large as 10 x 10 x 6 mm^3 were obtained, as indicated by Laue patterns taken on these samples. The orientation of the samples cut perpendicular to the growth axis was found to be close to [101]. The crystals of $RhSb_3$ were generally smaller than those of $CoSb_3$ but single crystals with dimensions of 5 x 5 x 2 mm^3 were obtained.

3.2. **Transport properties**

Samples in the form of disks of about 1 mm thick were cut from the single crystalline part of the ingots. In a cubic crystal structure such as the skutterudite, the transport properties are isotropic and no special attention was paid to the orientation of the samples measured. All as-grown samples are p-type with Hall carrier concentration in the 10^{16} to 10^{19} cm^{-3} range for $CoSb_3$ and between 2 and 7x1018 cm^{-3} for $RhSb_3$. It was found that, for the $CoSb_3$ ingots, the Hall carrier concentration of the samples decreases from the tip to the top of the ingots. Because the ingots were grown from non-stoichi ometric melts, during the growth the melt becomes richer in Sb and the stoi chi ometry of the samples could gradually change along the ingot, resulting in carrier concentration variations. These stoichiometric deviations might be very small and were not detected by EPMA as it was mentioned before. The addition of Te (between 0.1 and 0.2 at.%) into the original melts resulted in n-type samples.

Exceptionally high p-type Hall nobilities were obtained on $RhSb_3$ and $CoSb_3$ samples and are shown in Figure 2 which also shows the Hall nobilities of several state-of-the-art semiconductors as a function of the Hall canier concentration. The Hall mobilities of the two skutterudite compounds are significant y higher than those of Si, Ge and GaAs in the 10^{17} to 10^{19} cm^{-3} carrier concentration range. A maximum Hall mobility of about 8000 $cm^2.V^{-1}s^{-1}$ was obtained for $RhSb_3$ at a carrier concentration of 3.5 x $10^{18}cm^{-3}$. These high nobilities are consistent with the predominantly covalent bonding in the skutterudite structure and with the fact that the valence band is essentially derived from pnicogen-pnicogen bonds in these materials [1 O]. Figure 2 also shows the room temperature mobility of n-type $CoSb_3$ crystals doped with Te. The values compare well with the values for p-type GaAs and Si.

Figure 3 shows the high temperature Hall mobility values for $RhSb_3$ and $CoSb_3$ compared to those for Ge, Si and GaAs. The fall-off of the Hall mobility with temperature for the skutterudite compounds is not too pronounced. From the variations of the resistivity with temperature in the intrinsic regime, the band gap of $CoSb_3$ and $RhSb_3$ was estimated at 0.56 and 0,80 eV, respectively, Consequently, the intrinsic regime appears at a lower temperature for $CoSb_3$ than for $RhSb_3$. The high hole mobilities measured on the skutterudite compounds $CoSb_3$ and $RhSb_3$ even at high tern peratures make these materials interesting new semiconductors and we are pl anni ng further studies to investigate their thermoelectric and electronic properties.

4. conclusion

Large single crystals of the peritectic skutterudite compounds $CoSb_3$ and $RhSb_3$ were grown from Sb-rich melts by the gradient freeze technique. Characterization of the crystals by X-ray techniques and EPMA show the good quality of the materials. Hall effect and van der Paw measurements showed that the skutterudite compounds have exceptionally high hole nobilities and good electron nobilities for $CoSb_3$. These materials are interesting as new semiconductors and their thermoelectric and electronic properties should be investigated further.

Acknowledgments

The work described in this paper was carried out by the Jet Propulsion Laboratory/California Institute of Technology, under contract with the National Aeronautics and Space Administration. The authors would like to thank Jim Kulleck for the X-ray examinations and Paul Carpenter for electron probe microanalysis.

References

[1] N. Mandel and J. Donohue, Acts. Cryst. 1127(1971) 2288.

[2] T. Caillat, A. Borshchevsky, and J. -P. Fleurial, Proceedings of the Eleventh International Conference on Thermoelectric, Arlington, Texas, 1993, edited by K. R. Rao (University of Texas Press, Arlington, 1993).

[3] D. T. MorelIi, T. Caillat, J. -P. Fleurial, J. Vandersande, B. Chen, and C. Uher, submitted for publication to Physical Review B (1994).

[4] G. A. Slack and V. G. Tsoukala, J. Appl. Phys. 76 (1994) 1665.

[5] F. von Hulliger, HeIv. Phys. Acts 34 (1961) 783.

[6] D. Singh and W. Pickett., Phys. Rev. B50 (1 994) 11235.

[7] P, Feschotte and D. Lorin, Journal of the Less-Common Metals 155 (1989) 255.

[8] N. N. Zhuravlev, O. P. Gvan, and R. N. Kuzmin, Vestn. Mosk. Univ., Mat., Mekh., Astron., Fiz., Khim, 13, 5 (19S8) 79.

[9] A, Borshchevsky, T. Caillat, J. -P. Fleurial, NASA Tech Briefs, 18,3 (1 994) 68.

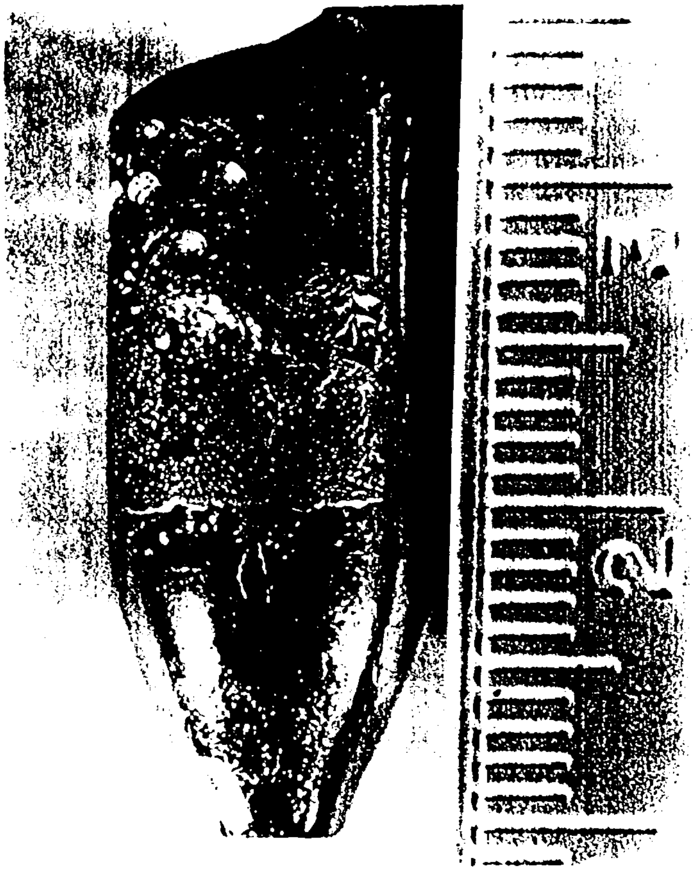
[10] D. Jung, M. H. Whangbo, and S. Alvarez, Inorg. Chem. 29 (1 990) 2252.

Figures captions

Figure 1. Single crystals of $CoSb_3$ grown by the gradient freeze technique (scale in centimeters).

Figure 2. Room temperature Hall mobility as a function of Hall carrier concentration for $CoSb_3$ and $RhSb_3$ single crystals. The values for Si, Ge and GaAs are also included for comparison.

Figure 3. High temperature Hall mobility for $RhSb_3$ and $CoSb_3$ single crystals and also Si, Ge and GaAs.



[illegible] Figure 1

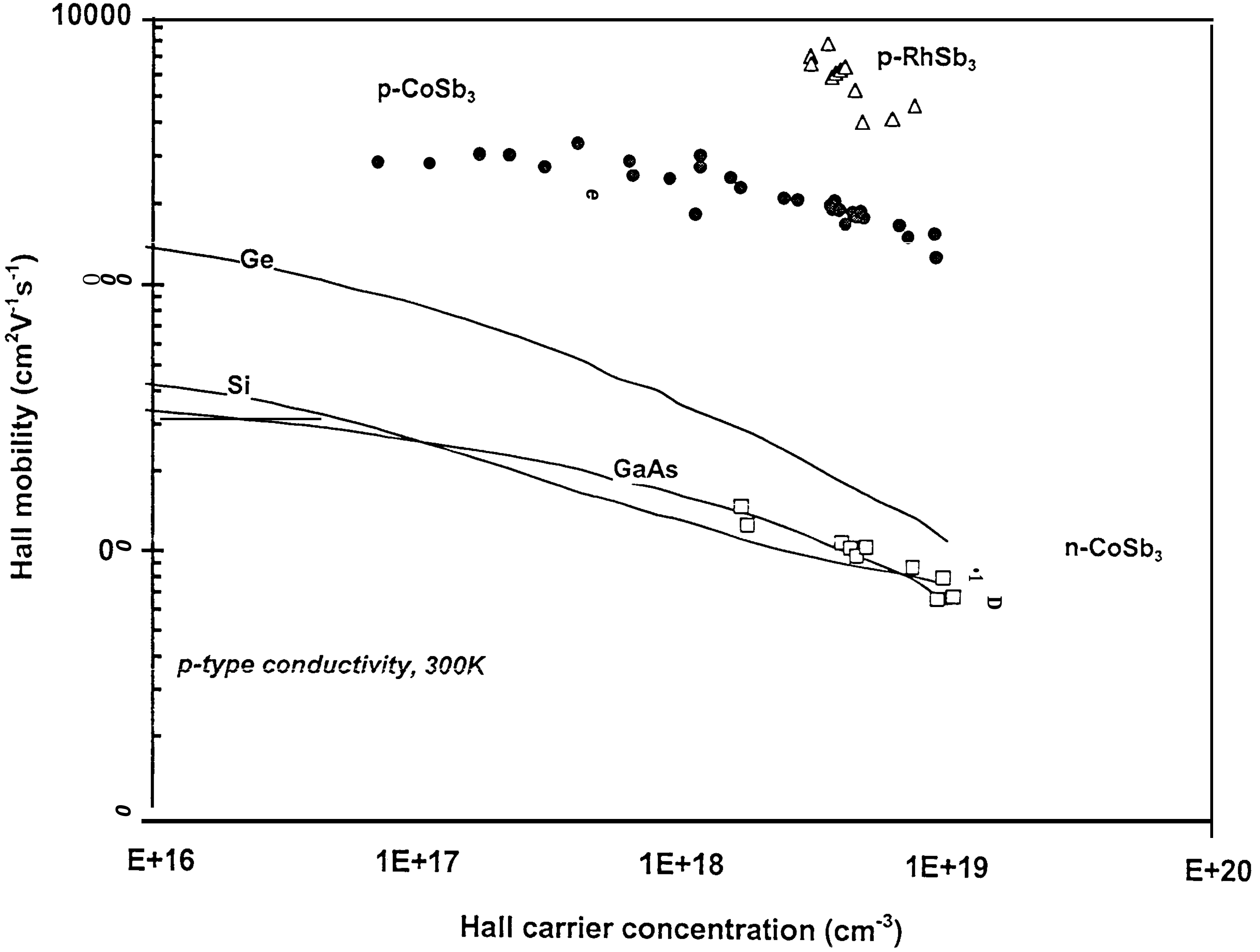


Figure 2 T Caillat

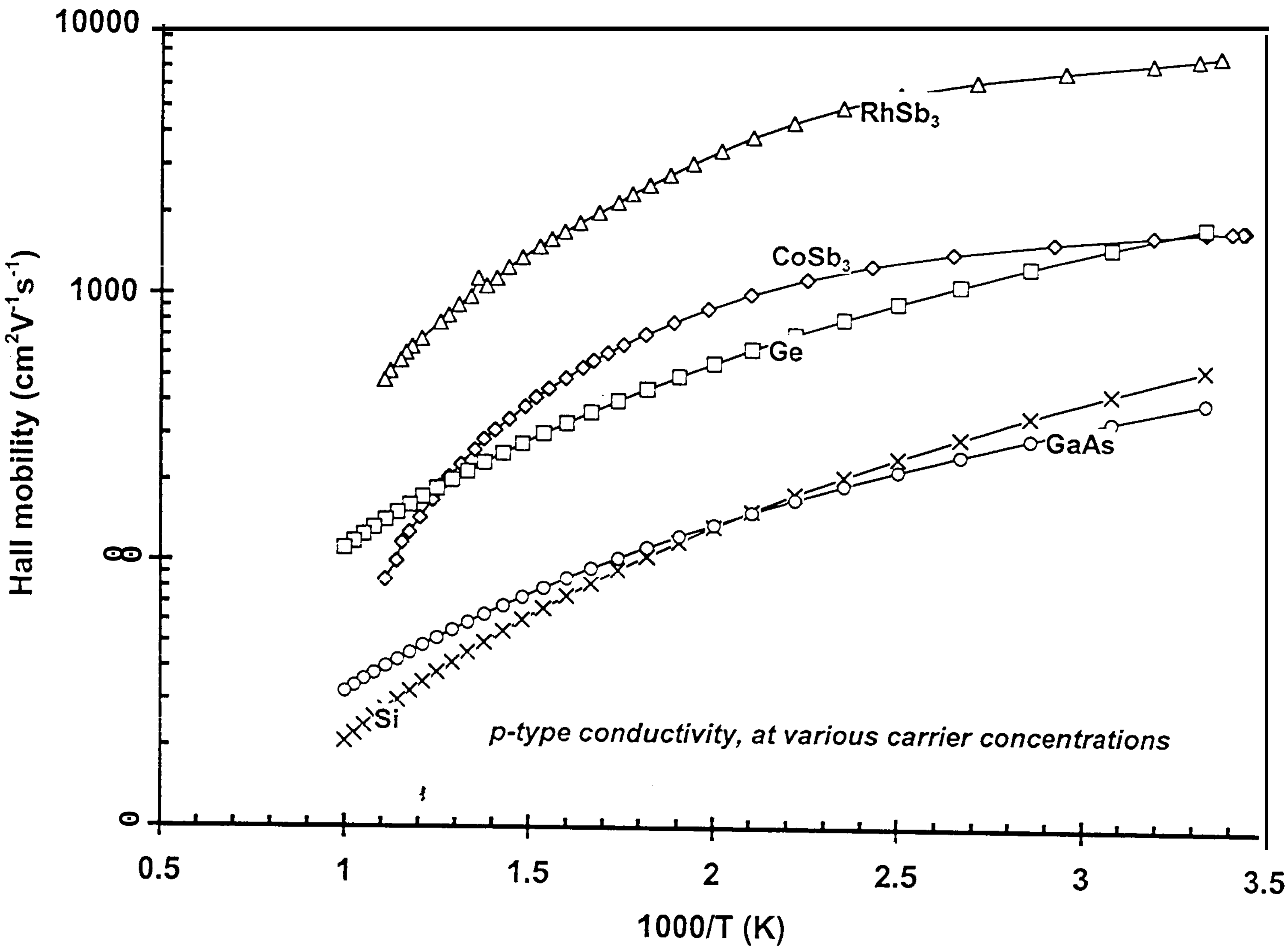


Figure 3 T Caillat